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O. G. Reznikova, A. B. Darintseva, I. B. Murashova

Chemical Technology Institute, 28 Mira street, 620002 Ekaterinburg

Phone: +7(343) 3754463; E-mail: a.b.darintseva@ustu.ru

About the stabilization of the dendritic structure of GG brand copper powder

In industry copper powder is recieved under constant current load. Surface roughening occurs during evolution of the dendritic particles. It is suggested to create a new impulse of current equal to the initial current density of 3200 A/m^2 in order to obtain uniform structure of the precipitate. Current load was evaluated by the result of chronopotentiometry research of the dynamics of the dendritic precipitate on cylindrical electrode. Four-impulse galvanostatic electrolysis was investigated for the copper powder GG. New current impulse shifts the electrode potential to the cathodic area, crystallization process flows more rapidly.

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Introduction

Electrolytic metal powders are widely used in many industries. Metal powders allow manufacturing by powder metallurgy products with unique characteristics[1]. In the industrial production of metal powders it is carried out while maintaining a constant current load which is several times higher than the limit. During the industrial electrolysis dendritic sediment was crystallized on cathodes. Properties of the finished powders depend on post-electrolysis processing: grinding, sieving, but the main characteristics of the powder are laid at the stage of electrolysis.

In galvanostatic electrolysis, sufficiently small particles are formed on the electrode surface that further either stop their growth or develop into dendrites. As the surface of dendritic sediment increases the diameter of the electrode with the sediment y thickness, cathode overvoltage of metal release is reduced[2]. With the decrease in cathode overvoltage diffusion limitations are reduced, the growth of dendritic sediment is suspended. It was stated[3] with the help of studies that achieving the field voltage equalling to 0,54-0,59 B leads to crystallization at the growth in front of solid globules, which are then fused to form a solid crust of a chained sediment. It is offered at certain points in time to submit a new electrode current pulse equal to the initial current density on the electrode. Increasing the

surge will lead to more intensive development of cathode surface on the growth front the thin branched particles will again start to crystallize[4]. With the development of dendritic sediment on the growth front, overvoltage will fall again; then it is necessary to submit a new current pulse on to the electrode.

The experimental part

Studies were carried out in an electrolyte solution to obtain a copper powder brand GG, which contains 23 g/l Cu^{2+} and 150 g/l H_2SO_4. Limiting stationary current density was determined using a potentiostat IPC-Pro by chrono-voltammetry with linear variation of the potential (Fig. 1).

According to the calculations steady-limit-stationary current density is $i_{PR.ST}$ = 370 A/m^2. Then we define the current load, which must be maintained at an electrode of diameter of 2.6 mm and a height of 8 mm. Electrolysis was carried out under laboratory conditions with a current density equal to the factory one, which is 3200 A/m^2, while it was necessary to set the current I = 226 mA. In the course of galvanostatic electrolysis, a continuous recording of growth of dendritic sediment was conducted with a video camera PanasonicSDR-S150GC-S. Electrolysis results are shown in Fig. 2.

When the current is on, overvoltage abruptly shifts to more negative values, followed by a period of small oscillations of the potential, which is followed by a period of large fluctuations. At the time of stopping of active growth of dendritic sediment (1440), overvoltage is significantly reduced. The diameter of the electrode with sediment is increasing until the overvoltage reaches the area of about 0.6 V, which is close to the precipitate ceases to lengthen.

Actively growing dendritic precipitate was decided to divide into 4 equal lengths of 6 minutes each. Through stated interval new current pulse was applied to the electrode, equal to the initial current density. For determining the magnitude current pulse, dynamics studies were conducted at two growth precipitate pulses of current (Fig. 3), three (Fig. 4) and four (Fig. 5).

Each subsequent pulse of current was calculated from the results of processing video precipitate dendritic growth. Current value was determined by the formula

$$I = i \cdot (d_0 + 2y)_t \cdot H,$$

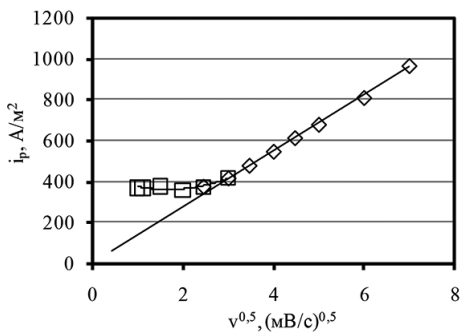

Fig.1. Dependence for the determination of the maximum steady-state current density

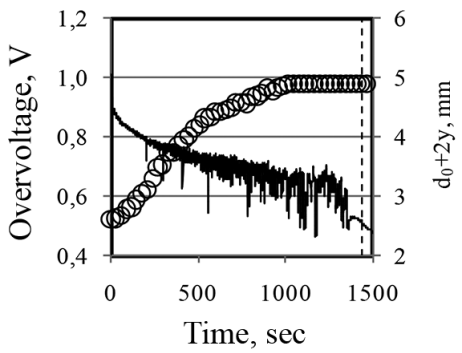

Fig. 2. Dynamics of changes in the diameter of the electrode with sediment (O) and cathodic overvoltage (line) in the single-pulse electrolysis

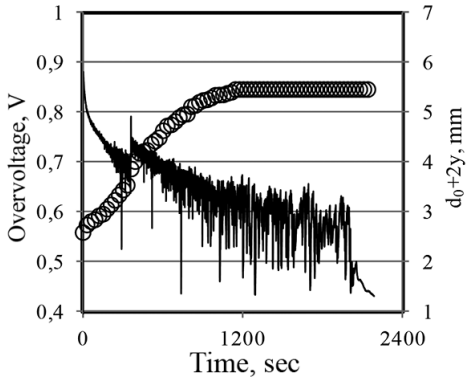

Fig. 3. Changing the diameter of the electrode with sediment (O) and cathodic overvoltage (line) during the two-pulse electrolysis

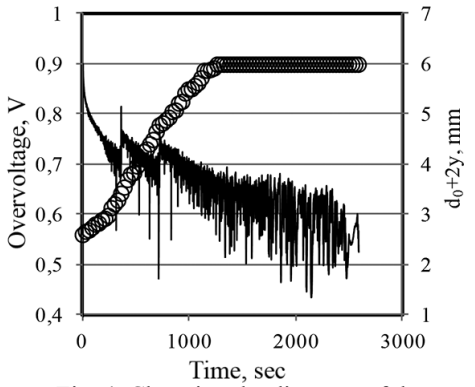

Fig. 4. Changing the diameter of the electrode with the precipitate (G) and cathode overvoltage (line) in the three-pulse electrolysis

where i is the initial current density of 3200 A/m^2; $(d_0 + 2y)_t$ is the diameter os an electrode with the sediment at the time of current; H is the height of the electrode, which is assumed to be constant, and equal to 8 mm. When there is 226 mA current after 6 minutes from start of the electrolysis, the electrode diameter was 3.73 mm (Fig. 2). In the second pulse at a given initial density, it was necessary to supply current of I = 335 mA.

At the time of switching current from 226 mA to 335, overvoltage abruptly increased from 0.68 to 0.79 V. When the same pulse electrolysis is used, the period of active growth was increased and amounted to 2100; the diameter of the electrode with a deposit at the time of stopping the process has reached 5.5 mm.

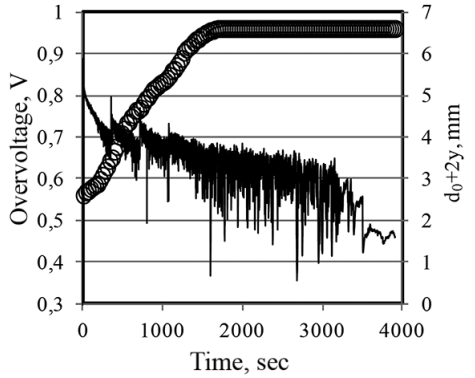

Fig. 5. Changing the diameter of the electrode with sediment (O) and cathodic overvoltage (line) during electrolysis four pulses

Two-pulse electrolysis further increases the time of active growth of dendritic solid (Fig. 4), the diameter of the pellet electrode is also increasing. According to the video processing of the growth of the dendritic precipitate after 6 minutes and after the second pulse current electrode had the diameter of 4.91 mm; therefore, the value of the third current pulse is 455 mA.

Galvanostatic electrolysis with three pulses of current (Fig. 4) increases the growth of the active sludge to 2500, the diameter of the electrode with the precipitate at the time the process is stopped is 6 mm. The magnitude of the current load on the fourth pulse is equal to I = 531 mA. Amperogram of four-pulse electrolysis is shown in Fig. 6.

Duration of four-staged electrolysis (Fig. 5) before the reset of the surge was 3900 sec; diameter of electrode with pre-

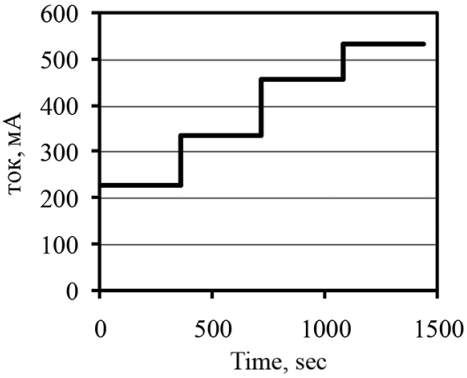

Fig. 6. Amperogram of four-pulse electrolysis

cipitation has increased to 6.6 mm.

Current pulse increases the cathode overvoltage; dendritic precipitate at the time of switching current begins to develop more actively. Increasing the current load leads to the rapid development of dendritic precipitate in height, which is characterized according to bend $d_0 + 2y$ (Fig. 3–5).

To study the structure of the sediment there were carried dendrit micrographs of thin cross-section of the electrode with the sediment (Fig. 7), made with a digital metallographic microscope AltamiMET 1M.

At the time of switching current pulse, more subtle elements of sediment are formed at the growth front. Fig. 7b shows a photograph of 1.5 min after the third switching current.

Cylindrical electrode with dendrit sediment is 3D electrode. The surface of the three-dimensional electrode works unevenly, electrochemical process occurs on the outer surface of the active electrode. Speed of electrode process decreases from the outer surface into the thickness of the sediment. The penetration depth λ is the characteristic length of the distance which the speed of the process is reduced by 2.7 times.

The penetration depth of the electrode process was calculated from the results of processing of the chronopotentiograms and videos dendritic growth of sediment (Fig. 8).

When the new current pulse is sent, overvoltage increases abruptly but does not reach its maximum value at the previous pulse. This phenomenon is due to the different penetration depth of electrochemical process in the dendritic layer of sediment.

The depth of penetration is defined as half the difference of electrode diameter with sediment at the maximum overvoltage when switching less electrode diam-

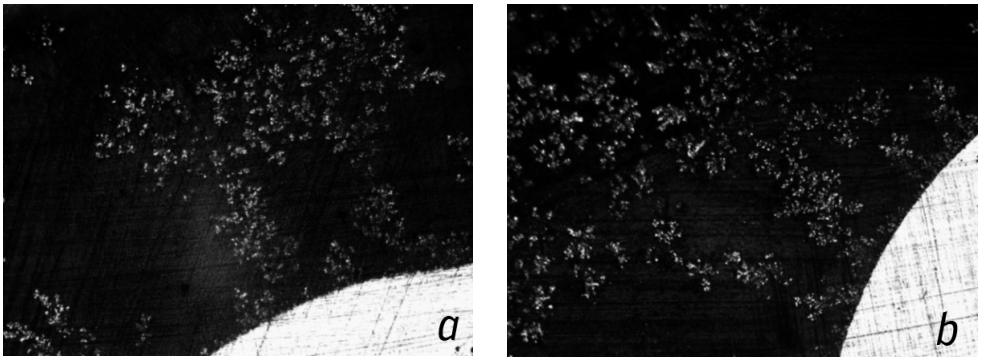

Fig. 7. Micrographs of a cross section of the electrode with dendritic precipitate. Electrolysis time, min: *a* – 18; *b* – 19.5. increase x10

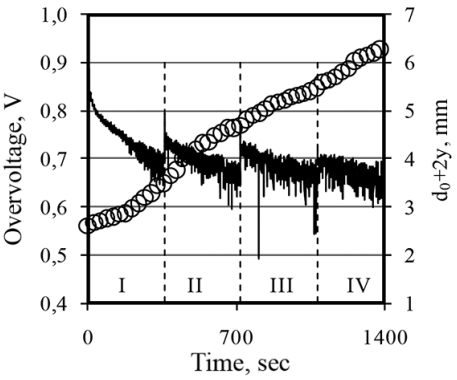

Fig. 8. Chronopotentiogram (line) and the diameter of the electrode with the precipitate (a) at four-pulse electrolysis. The numbers in the diagram show the number of periods

eter with sediment, corresponding to the value of surge suppressors, equal to the maximum by setting the previous current pulse. For a given current pulses λ was calculated. At current load of 335 mA

$\lambda_{335} = 0,5 \cdot (3,48 – 2,68) = 0,4$ mm;

at 455 mA

$\lambda_{455} = 0,5 \cdot (4,68 – 3,49) = 0,595$ mm;

at 531 mA

$\lambda_{531} = 0,5 \cdot (5,47–4,74) = 0,365$ mm.

Unambiguous results in penetration depth values could not be obtained. At the same conductivity of electrolyte solution, the specific surface area of the electrode displaced electro-chemical process on an outer surface of a porous electrode in the case of a larger current[5].

Results and discussion

Increasing the load current to create the initial current density on the growth front of sediment raises cathode overvoltage, accelerates the process of elongation of dendrites and again leads to the crystallization of thin branched particles. Using this mode of the process a significant increase in sediment build-up period can be achieved, while maintaining its structure.

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